

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of

HYE KYUNG C. TIMKEN

Serial No.: 10/728,641

Filed: December 5, 2003

For: HOMOGENEOUS MODIFIED-
ALUMINA FISCHER-TROPSCH
CATALYST SUPPORTS

GROUP ART UNIT: 1754

EXAMINER: Cam N. Nguyen

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DECLARATION UNDER 37 CFR 1.132

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

NOW COMES Hye Kyung C. Timken who declares and says:

1. I am the inventor of the subject matter claimed in the above-identified patent application. I received a Ph.D. degree in chemistry from the University of Illinois in 1987. I also received a M.S. degree in Chemistry from the Yonsei University in Seoul, Korea in 1981 and a B.S. degree in LAS from the Yonsei University in 1979.

2. I have studied and/or worked in the field of porous materials synthesis, characterization of materials, scale-up of new materials, and catalytic evaluations since 1983.
3. I have been employed by Chevron Energy Technology Company ("ETC") (an affiliate of the assignee of the subject patent application) for approximately 7 years. I work in the field of catalysis (porous materials synthesis, characterization of materials, scale-up of new materials, and catalytic evaluations).
4. I have reviewed the Office Action of May 26, 2006 in the above-identified application and the references cited therein and most particularly U.S. Patent No. 4,988,659 to Pecoraro.
5. I have extensive experience in silica-alumina preparations in the ETC laboratory as well as at commercial plants and found that mixing of the viscous alumina and silica solutions to obtain a homogeneous state of sol and gel is often very difficult and further that a conscious effort is necessary in order achieve homogeneity even assuming that the person doing the mixing knows that a homogeneous state is desired. Just stirring vigorously will often not achieve a complete mixing, which is necessary to produce a catalyst support in which the modifying metal oxide is homogeneously distributed throughout the base metal oxide as is claimed in the above-identified patent application. The Pecoraro reference does not even recognize that complete mixing or homogeneity is desirable.
6. Pecoraro Example 1 uses a very heavy, viscous mixture. In my opinion, the mixing times specified in Pecoraro Example 1 would not result in

complete mixing and as a consequence a homogeneous distribution of the modifying-metal oxide throughout the base-metal oxide.

7. I conducted the following procedure, which is similar to Pecoraro Example 1 with respect to the quantity of material and mixing times. This evidence supports my opinion in Paragraph 7 above. The procedure was as follows:

An acidic aluminum solution (Solution I containing 7.3 wt% Al_2O_3) was prepared by dissolving 98.8 kg of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and 18.6 kg of acetic acid (99.9% concentrated) in 168.4 kg of deionized water. A dilute solution of sodium silicate (Solution II containing 5 wt% SiO_2) was prepared by diluting 84.5 kg of concentrated sodium silicate solution (contains 29wt% SiO_2 and 9% Na_2O) with 371.6 kg of deionized water. The silicate solution was gradually added to the aluminum solution while vigorously mixing to prepare Solution III. It took about 80 minutes to add the silicate solution to the aluminum solution. The final pH of the combined solution (Solution III) was 1.6, and the mixing produced a clear silica and alumina solution. The final Solution III contained

$$\begin{aligned}\text{SiO}_2/\text{Al}_2\text{O}_3 \text{ molar ratio of } 2.0 \\ \text{H}^+/\text{Na}^+ \text{ molar ratio of } 1.25\end{aligned}$$

Diluted ammonia solution (Solution IV containing 14 wt% NH_3) was prepared for gellation. The diluted ammonia solution was added gradually to Solution III containing silica and alumina sol while vigorously mixing. Cogelled silica-alumina started to precipitate when the pH of the slurry reached at about 3.0. We continued the ammonia solution addition until the pH of the slurry reached 8.0. It took about 57 minutes to complete the gellation and a total of 45.2 liter of dilute ammonia solution was consumed. The gel slurry was aged at room temperature for 3 hours while stirring. We added a small amount of dilute ammonia solution during the aging to maintain the pH at 8. The fact that we had to add ammonia solution shows again that Solution III was not homogeneous and pH was changing. This cogelled silica-alumina was filtered to

produce a filtered cake. The filtered cake was slurried with some additional deionized water and spray dried. The spray-dried material was washed with a hot solution of ammonium acetate (3.8 wt%, ~ 10 vol/vol solutions, 140 °F) for 15 minutes, and then rinsed with excess of deionized water. The washing step was repeated four more times. The washed spray dried sample was dried at 250°F overnight, and then calcined under excess dry air at 1000°F for 1 hour for activation. Physical properties of the final silica-alumina are:

Surface area, m²/g 360
Total pore volume, cc/g 0.66
Surface to Bulk Si/Al Ratio 0.86
% crystalline alumina phase by XRD 7.2 %

8. In conclusion, it is my opinion based on the foregoing data and my knowledge relating to the preparation of silica-alumina that the procedure of Pecoraro Example 1 will not produce a silica-alumina composition having a surface-to-bulk Si/Al ratio of from 0.9 to 1.1.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of this application or any patent issued thereon.


Hye Kyung C. Timken

Nov. 16, 2006

Date